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## De kristalstructuur van H5IO6 en HI3O3. Een onderzoek met roentgen-en neutronenstralen

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*Document Version*

Publisher's PDF, also known as Version of record

*Publication date:*

1963

[Link to publication in University of Groningen/UMCG research database](#)

*Citation for published version (APA):*

Feikema, Y. D. (1963). *De kristalstructuur van H5IO6 en HI3O3. Een onderzoek met roentgen-en neutronenstralen*. s.n.

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## SUMMARY

### Results

Various iodic acids have been determined but information about their structures has been rather scanty. Only the structure of  $\alpha$ -HIO<sub>3</sub> was known when we started the determination of the structure of H<sub>5</sub>IO<sub>6</sub> and HI<sub>3</sub>O<sub>8</sub>. The oxidation numbers of iodine in these compounds are +7 and +5 respectively.

A knowledge of the position of the hydrogen atoms was likely to be essential for the interpretation of these structures. Therefore, after a preliminary X-ray study, we made use of neutron diffraction for the structure determination of H<sub>5</sub>IO<sub>6</sub>. It was found that the crystals consist of molecules O=I(OH)<sub>5</sub> in which the distance I=O is 1.79 Å and in which the average I—O and O—H distances are 1.89 and 0.89 Å respectively, subject to standard errors of 0.02 and 0.03 Å in the individual bond lengths. Iodine is octahedrally surrounded by oxygen atoms, the valence angles I—O—H are about 112°. All hydrogen atoms are engaged in hydrogen bonds to oxygen atoms of neighbouring molecules, which explains the small thermal motion ( $B_I = 1.05$ ,  $B_O = 1.65$  and  $B_H = 2.80 \text{ Å}^2$ ) at room temperature. The average lengths of the hydrogen bonds are 2.78 and 2.60 Å for bonds directed to single and double bonded oxygen respectively.

The structure of HI<sub>3</sub>O<sub>8</sub> has been determined by X-ray diffraction only. However, a large number of reflexions were measured and the parameters, including anisotropic thermal motion for the iodine atoms, were carefully refined by least squares analysis. In this way the position of the iodine and oxygen atoms could be determined with standard errors of about 0.0007 and 0.010 Å respectively. The rather high accuracy obtained for the positions of oxygen atoms in the presence of the heavy iodine atoms made it possible to deduce from the I—O bond lengths the position of the hydrogen atom in an indirect way, because the hydrogen atom should be attached to a single bonded oxygen atom (I—O about 1.90 Å). It appeared that HI<sub>3</sub>O<sub>8</sub> should be written I<sub>2</sub>O<sub>5</sub>·HOIO<sub>2</sub> as had been expected from infrared studies by Dupuis and Lecomte (1961). The I<sub>2</sub>O<sub>5</sub> molecules, shown in figure 19, have the structure (O=)<sub>2</sub>I—O—I(=O)<sub>2</sub> with average I=O and I—O bond lengths of 1.79 Å and 1.96 Å respectively with a standard error of 0.013 Å in the individual values. The valence angles at the iodine atoms are about 94°, the valence angle at the oxygen bridge is 125.8°. The H—O—I(=O)<sub>2</sub> molecules in the structure have essentially the same shape as in  $\alpha$ -HIO<sub>3</sub>; we found for the I=O and I—O bond lengths 1.80 and 1.90 Å respectively (standard error 0.013 Å) and for the

O—I—O bond angles about  $96^\circ$ . The hydrogen atom was assumed to be linked to the oxygen atom involved in the long I—O bond. It is seen that in the  $\text{HI}_3\text{O}_8$  structure each iodine is chemically bonded to three oxygen atoms. In addition there seems to be an exceptionally strong intermolecular interaction between iodine and three (or four) other atoms since the I...O distances are roughly 1 Å smaller than the sum of the Van der Waals radii of iodine and oxygen. These intermolecular interactions explain the extremely small thermal motion in  $\text{HI}_3\text{O}_8$  ( $B_{\text{I}} = 0.55$  and  $B_{\text{O}} = 1.15 \text{ Å}^2$ ), which cannot be caused by hydrogen bonds as in the case of  $\text{H}_5\text{IO}_6$ .

## Methods

### *a. X-ray study of $\text{H}_5\text{IO}_6$ and $\text{HI}_3\text{O}_8$*

Both compounds belong to the spacegroup  $\text{P2}_1/\text{n}$  and have four molecules in the unit cell. The crystal data are listed in table 2 and chapter IV § 1 respectively.

All intensities were recorded on integrated (equi-inclination) Weissenberg photographs, taken with Zr filtered Mo radiation. For  $\text{H}_5\text{IO}_6$  the intensities of the  $hk0$ ,  $h0l$  and  $0kl$  reflexions were measured; during this preliminary investigation no correction for absorption was applied. For  $\text{HI}_3\text{O}_8$  about 2500 independent reflexions  $hkl$  were measured from different layer lines about the  $b$  axis and from the zero layer lines about the  $a$  and  $c$  axes. The reflexions were corrected for absorption ( $\mu_{\text{R}} = 141 \text{ cm}^{-1}$ ); in calculating the path lengths for the higher layer lines about the  $b$  axis the crystal was assumed to be infinitely long in the  $b$  direction.

In both cases the approximate structure, except the positions of the hydrogen atoms, could be determined from projections. First the coordinates of the iodine atoms were found from Patterson maps; the oxygen atoms could be found by applying the vector convergence method and/or by calculating error syntheses from which the contribution of the iodine atoms had been eliminated.

The structure of  $\text{H}_5\text{IO}_6$  has been refined isotropically by a least squares analysis of the reflexions  $hk0$  and  $0kl$ . The final values of the reliability indices are 0.08, 0.12 and 0.08 for the observed  $hk0$ ,  $h0l$  and  $0kl$  reflexions respectively. The final coordinates are listed in table 11, the parameter  $B$  in the temperature factor  $\exp[-B(\sin \theta/\lambda)^2]$  is  $0.80 \text{ Å}^2$  for iodine and  $1.15 \text{ Å}^2$  for oxygen.

The structure of  $\text{HI}_3\text{O}_8$  has been refined by a least squares analysis of the three-dimensional data; for the iodine atoms anisotropic thermal parameters have been taken into account. The reliability index is 0.056; the final parameters are listed in table 14.

### *b. Neutron diffraction study of $\text{H}_5\text{IO}_6$*

The principles of neutron diffraction and the neutron diffractometer used in this investigation are described in chapter III. The intensities of

127  $hk0$  and 124  $0kl$  reflexions were measured from crystals of dimensions  $4 \times 4 \times 4$  and  $4 \times 4 \times 8$  mm<sup>3</sup> respectively. It appeared that only a few reflexions were largely in error by extinction.

Approximate positions of the hydrogen atoms were obtained from error syntheses from which the contribution of the iodine and oxygen atoms, as found from the X-ray study, had been subtracted. During the refinement by a least squares analysis of the reflexions  $hk0$  and  $0kl$ ; anisotropic thermal parameters were taken into account for all atoms. The reliability indices are 0.064 and 0.061 respectively. The final anisotropic thermal parameters are listed in tables 8 and 10; the final coordinates in table 11.